RADIOFREQUENCY ELECTRODELESS SYNTHESIS OF POLYMERS: REACTION OF CO, N_2 AND H_2

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Introduction

A certain amount of the large literature concerning the synthesis of compounds in electrical discharges relates to the synthesis of polymeric materials, and many industrial patents exist in this category. Most of these syntheses have employed 1) hydrocarbon reactant(s) or 2) discharge apparatuses involving internal electrode configurations as the source of excitation, and the glow discharge or "cold plasma" was initiated by a. c. or d. c. fields of several hundred volts between the internal electrodes (1).

We wish to report an electrodeless discharge synthesis of a polymeric material involving the simple inorganic gases CO, N_2 and H_2. The advantages of the electrodeless technique are principally avoidance of electrode erosion or kinetic interaction of the electrodes with the reacting gas mixtures, the capability of filling uniformly a plasma reactor with a volume of excited gas, and engineering advantages of radiofrequency excitation.

Experimental

Run Procedure

An apparatus for precision metering of several gases into plasma reactors was designed and constructed for this work. Figure 1 shows the system design. Up to four different gases may be metered individually at known flowmeter pressures. Since the gases were non-corrosive, mercury manometers adequately served as the flowmeter pressure measurement device. Flows of gases in $cm^3\ min^{-1}$ NTP were calculated from the gas viscosity at the operating temperature, the gas density at the operating pressure and temperature, and the flowmeter scale reading. The flowmeter operating pressure P_{FM} was calculated from $P_{FM} = \Delta P + P_{SYS}$ where P_{SYS} is the system pressure measured at Point A and ΔP is the differential pressure across the manometer.

The accuracy of flow rates are taken to be ± 2% to ± 10% depending on flow meter condition and flow rate. In nearly every case, the ± 2% accuracy was maintained. The reagent gases, sources, and statement of purity are as follows:

Gas	Grade	Source	Purity
CO	C. P.	Matheson	99.5%
N_2	Extra Dry	"	99.7%
H_2	Pre-Purified	"	99.95%
CO_2	Coleman	"	99.99%

After calculations of the desired flow rates and consequent required flow conditions, the entire gas line is purged by alternate pumping and filling with the desired gases. The metering valve V(2) and the flow meter pressure regulating valve V(3) are adjusted to provide the conditions of flow meter pressure P_{FM} and flow meter indication necessary to produce with accuracy the desired flow-rates. Leak checks

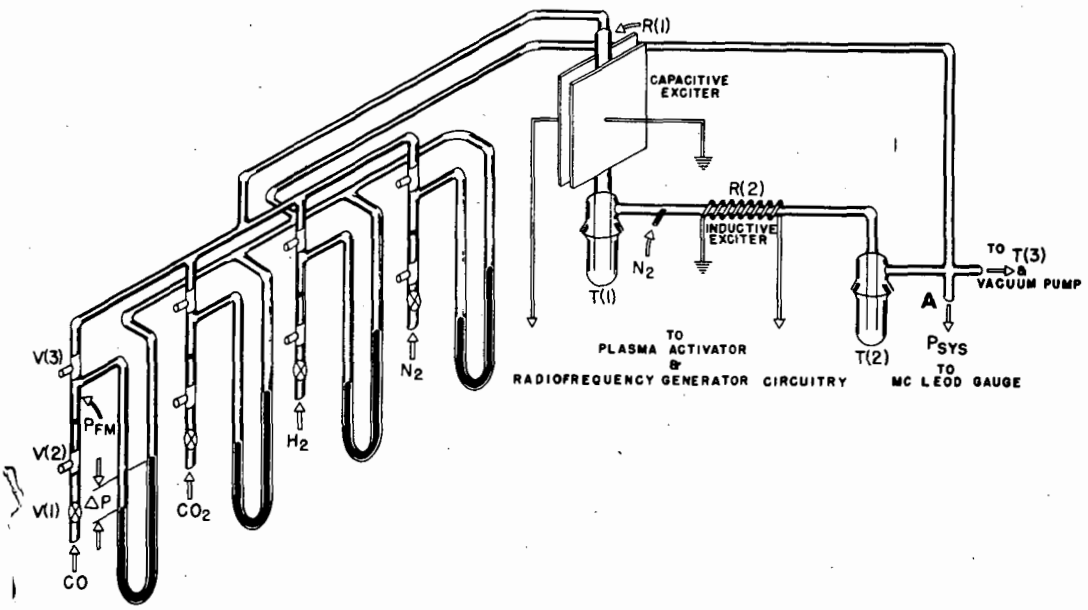

Fig. 1 Schematic of flow discharge apparatus and gas monitoring system.

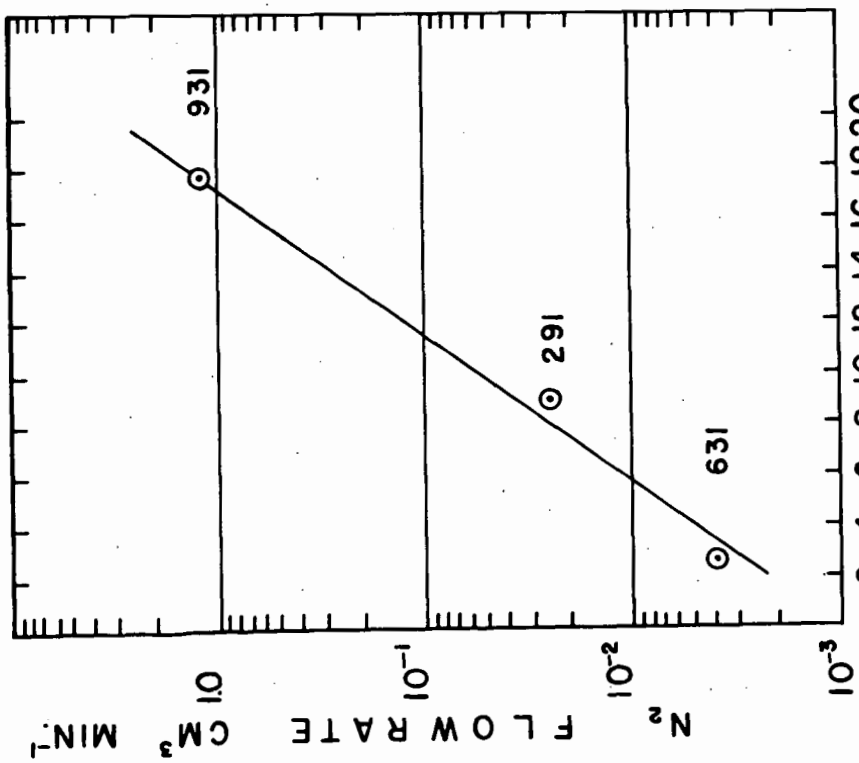

Fig. 2 Dependence of nitrogen found in polymer on nitrogen flow rate.

with a helium mass spectrometer leak detector are made before and after the experimental run. Valve V(1) is a gas flow on-off valve.

With the flow rates accurately adjusted, the RF Generator/RFG-600 (see below) connected to the capacitive exciter is energized and the activator tuned while bringing the generator to maximum power, ~ 300 watts. Trap T(1) which is filled with 3 mm diameter glass beads and some pyrex wool to assure efficient trapping is chilled with liquid nitrogen. Traps T(2) and T(3) are chilled respectively with a dry ice/2-propanol slurrey and liquid nitrogen. T(3) contains 5 mm glass beads again to assure efficient trapping and to assure non-interference from vapors originating from the pump. Next, the second RF generator/RFG-600 connected to the inductive exciter is energized and the activator tuned while bringing the generator to maximum power, ~ 300 watts.

With the gases and flows selected for the experiment, the reaction proceeds and the polymer is allowed to accumulate along with the other products. After running a length of time, the generators and gas flows are turned off and the traps allowed to warm up. The pump is then valved off and the system let up to atmosphere with Argon. The polymer of interest is removed from the inner surface of the center tube of T(2) and retained for analysis.

Radiofrequency Equipment

The two plasma reactors were each activated either capacitively or inductively with RF generators (RFG-600, Tracerlab, Inc.) with deliverable power from minimum up to 300 watts. The generators consist of an RF section composed of a two stage system utilizing a crystal controlled oscillator, and a Class C power amplifier stage. The second part is a power supply producing plate, screen, bias, and filament power. The details of the electronic requirements for generation and transmission of RF energy have been described elsewhere (2).

Energy from the generator is transmitted to the exciter plates R(1), or coil, R(2) via a plasma activator, the circuitry of which allows maximization of the RF energy to the gas load and minimization of the reflected power back to the generator. A great experimental advantage of this means of power delivery and measurement is the ability the operator realizes in being able to reproduce his discharge conditions for the different experiments or from run to run. The net power delivered by the generator is a function of gas type and concentrations, which in turn are related to system pressures and flow rates. Each time an excited gas parameter is changed, there is a concomitant change in the intrinsic impedance of the gas load, which must be rematched to the impedance of the secondary activator circuits. Thus, the convenience of simply being able to achieve this matching by the power meter on the generator, which reads forward and reflected power, is a decided advantage.

All experiments were carried out at a radiofrequency of 13.56 MHz ±6.87 KHz, an FCC approved non-interference band. The choice of inductive vs. capacitive exciters for R(1) and R(2) was rather arbitrary, both were employed to test any significant differences in the reactions induced. The conclusion is that the chemistry is independent of the mode of excitation. There are, however, definite advantages either configuration offers in certain systems, such as gas-solid reactions. This has been described in Ref. (2).

Observations and Discussion

Synthesis

The polymers to be described below can be produced either of two ways: (1) the reaction directly of CO, H_2, and N_2; or (2) the reaction first of CO_2 and H_2 to produce CO, via the water gas reaction, and then subsequent reaction of the produced

CO, with excess H_2, and N_2 admitted either downstream of T(1), as indicated in Fig. 1, or in the manifold system. The latter experiment was believed to be a purer source of CO and was employed for most of the preparations. The liquid nitrogen temperature of T(1) and its packing trapped all significant water produced in the water-gas reaction, as well as remaining CO_2. It became apparent that if T(1) does not trap all the significant water, that no polymer forms at T(2), due either to a reaction of H_2O or discharge products therefrom (3) with polymer precursors, or to the interference of water to the deposition of the polymer as a film on the cold inner tube of T(2).

The polymers at low N_2 flows are characterized by being transparent, yellow, tightly adherent films. At higher N_2 flows, the transparency decreases, and film strength appears to decrease, indicating perhaps lower molecular weight materials being formed.

The production of the polymer under the flow conditions listed in Table I appears critically dependent on the system pressure. In the experiments, the flows of CO or CO_2 and H_2 were maintained at nearly constant values while the nitrogen flow rate was varied. The very low flow rates of N_2 resulted from permeation through a very short segment of Tygon tubing initially connecting R(1) to the manifold outlet. These rates of permeation were measured by observing rates of system pressure increases with time, and checked by He permeation with the mass spectrometer at the same point. In Run 861, the uncertainty is probably an order of magnitude; in Runs 631 and 291, the uncertainties are half that. In any case, the low flows of N_2 in the initial experiments were much less than measured flow rates in subsequent experiments, which indicate (Table I) that less and less polymer is produced (other gases fixed) as the N_2 flow rate increases. At a very high N_2 flow, ca. 107 cm^3 min^{-1}, no polymer was observed to form at all.

TABLE I. Flow Conditions for Several Sample Preparations

Run	Flow Rates, cm^3 min^{-1}				P_{SYS}, torr	Power, Watts		Run Time, Mins.
	CO_2	CO	N_2	H_2		R(1)	R(2)	
861	1.18	---	$\sim 3.1 \times 10^{-6}$	3.65	.310	330	355	680
631	1.43	---	3.9×10^{-3}	3.95	.320	---	280	414
291	----	2.18	$\sim 2.5 \times 10^{-2}$	4.43	.36	300	---	720
931	1.25	---	1.26	3.60	.45	320	350	463
991	1.36	---	9.88	3.83	.75	320	410	460
890	1.36	---	107	3.74	2.47	320	360	273

Table II indicates elemental analyses for C, H, N, and O for several runs. The per cent nitrogen is found to increase as the flow of N_2 increases. This suggests, up to a certain point, that one can produce in this experiment tailored polymers containing a controllable amount of a given constituent by controlling its flow rate. The dependence of per cent nitrogen found in the polymer on flow rate is given in Figure 2.

Why no polymer forms at high system pressures, ca. 1.0 mm Hg pressure, is perhaps due to competing gas phase processes (4). The same types of polymers no doubt may be arrived at by substitution of ammonia for the N_2 - H_2 mixture, since one often achieves many similar results irrespective of whether one uses $N_2 + H_2$ or NH_3. Little molecular or atomic oxygen, as such, should be produced in these

discharge reactions producing the polymer film. If any appreciable amount were present, this would readily oxidize the polymer, since we typically clean up our system of all organic products using an oxygen discharge.

TABLE II. Elemental Analysis for Several Typical Preparations

Run	% Element Found				Total
	C	H	O	N	
861	80.51	10.31	8.06	0.2	99.1
631	75.0	9.5	12.7	2.8	100.0
291	68.19	9.12	13.23	8.84	99.38
931	55.90	7.77	18.40	17.64	99.71
991	very little formed				
890	no polymer formed				

Spectroscopy

The transmission infrared (Fig. 3) and internal reflectance, ATR (Fig. 4) spectra for samples 291 and 633, respectively, show very nearly identical features for the principal bands. Structural moieties such as

$$-\overset{\overset{O}{\|}}{C}-NH_2,\ -CH_2-,\ -CH_3,\ C-N,\ C{=}N,\ \text{and}\ -OH$$

in organic compounds give the best comparative infrared spectral features to those observed for the synthesized polymer. Spectra of polyacrylamides, polyacrylonitriles and proteins (5) of some types, give quite similar spectra. Carbon-nitrogen double or single bonds may exist in the synthesized polymer, but there is no evidence for the strong $-C{\equiv}N$ frequency at ca. 2240 - 2260 cm^{-1} (5). Nicholls and Krishnamachari (6) found in microwave electrodeless discharges at 2450 MHz emission bands of NCO formed at cryogenic temperatures from the reaction

$$N(^2P) + CO\ (X\,^1\Sigma^+) \rightarrow NCO \begin{cases} A^2\Sigma^+ \\ B^2\Pi_i \end{cases}$$

at the cold surface. Thus an NCO species may enter into the polymer as an important structural entity in the present case.

Conclusions

Under the flow discharge conditions of this study, the RF electrodeless method appears to offer interesting synthetic possibilities with the simple inorganic gases. One might better understand the mechanism of origin of some polymers as a function of simple excited molecular, atomic or free radical precursors, generated in the discharge. The composition of the gas phase products formed in various reactions would be worth monitoring. Some of the gas products in the present study are being analyzed.

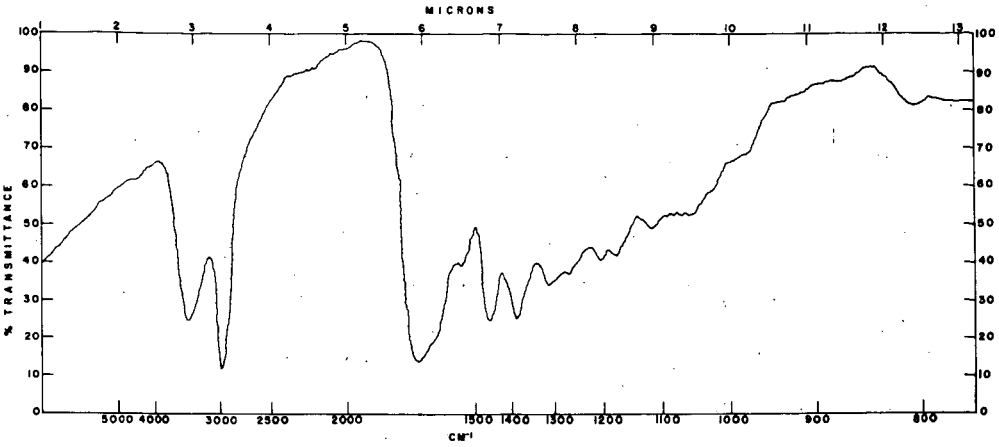

Fig. 3 Infrared transmission spectrum of polymer, Run 291.

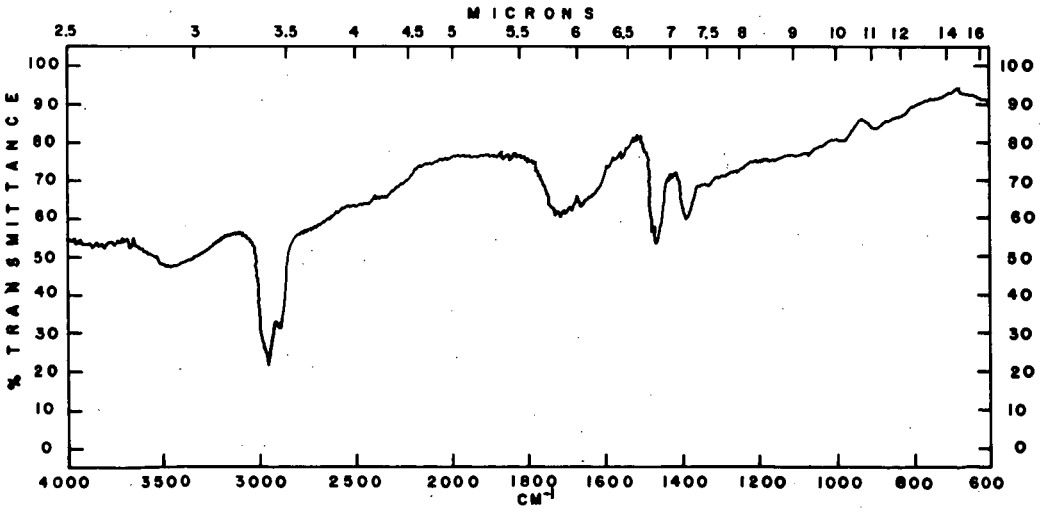

Fig. 4 Infrared ATR spectrum of polymer, Run 633.

Acknowledgement

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